EOD TEST PROCEDURE

TP 116B	
Title Analysis of Sulfur in Petroleum Fuels by X-Ray Fluorescence	**Page Number** 1 of 23
Originator Bruce Kolowich	**Supersedes** TP 116A
Responsible Organization Fuels and Chemical Analysis Branch	**Computer Program** Instrument Software
Type of Test Report Instrument-Generated Sample Analysis Report	**Data Form Number** None
Report Distribution Chem Lab Results File	**Implementation Date** 09-30-94

Implementation Approval

Original Test Procedure Authorized by EPCN #157 on 05-03-94

Revision Description

(1) The purpose of this change is to revise the procedure as described in EPCN #169.

Note: Specific brand names in EPA/EOD procedures are for reference only and are not an endorsement of those products.

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Attachments

1. Purpose

(1) This test procedure covers the determination of total sulfur in diesel fuel or gasoline. It is the Engineering Operation Division (EOD) version of American Society for Testing and Materials (ASTM) Standard D 2622, Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry.

This specific procedure has been written for samples in the range of 0.002%-0.50% sulfur in diesel fuel, or 10 ppm-1500 ppm in gasoline, both on a weight basis (w/w). The working range of this procedure may be extended up to 5.0% by calibrating with additional, higher-concentration standards.

2. Test Article Description

(1) Diesel fuel samples of at least 20 mL, containing 0.002%-0.50% (w/w) sulfur, or gasoline samples of at least 20 ml, containing 10 ppm-1500 ppm (w/w) sulfur

Samples containing higher levels of sulfur may also be diluted for analysis.

3. References

3.1 ASTM Standard D 2622, "Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry"

3.2 ASTM Standard Practice E-177-86, "Standard Practice for the Use of the Terms Precision and Bias in ASTM Methods"

3.3 ASTM Manual MNL7, "Manual on Presentation of Data and Control Chart Analysis: 6th Edition"

(1) 3.4 40 CFR 80.2, as published in the Federal Register, Tuesday, August 21, 1990, Vol. 55, No. 162, p34137

40 CFR 80.46, as published in the Federal Register, Wednesday, February 16, 1994, Vol 59, No. 32, p7826

3.5 Rigaku Instrument Manual, Rigaku Software Manual

3.6 Fuels and Chemical Analysis Branch (FCAB) Chemical Hygiene Plan, Appropriate Material Safety Data Sheets, and the FCAB Chemical Inventory

4. Required Equipment

4.1 Rigaku 3271 X-Ray Spectrometer, equipped for soft x-ray detection in the 5.37 Å range

For optimum sensitivity to sulfur, the instrument should be equipped with the following:

4.1.1 Optical path of helium

4.1.2 Pulse-height analyzer or other means of energy discrimination

4.1.3 Detector designed for the detection of long wave-length x rays

4.1.4 Analyzing crystal, suitable for the dispersion of sulfur K_{α} x rays within the angular range of the spectrometer employed

For this analysis, a germanium crystal will be used.

4.1.5 X-ray tube, capable of exciting sulfur K_{α} radiation

For this analysis, a tube with a rhodium anode will be used.

4.2 Di-n-Butyl Sulfide (DNBS)

This is a high-purity standard material rated 96% or higher purity, confirmed to be at least 99% pure.

A DNBS sample with certified analysis designed specifically for this analysis is also acceptable as a source of DNBS. If this material is used for calibration, the certified sulfur concentration should be used to calculate the weight fraction sulfur in the prepared standards.

Note: Although 96% is the highest guaranteed purity available commercially for DNBS, in practice the actual purity is much higher. Before beginning calibration with a new bottle of DNBS, it should be analyzed by gas chromatography (GC) using a flame ionization detector (FID) to establish its purity. A general analysis with a slow ramp is preferred, with an integration format of normalized area percent. With this method, a result indicating more than 2% area impurities would indicate a suspect standard material. Using this setup for GC, a 2% area for impurities would roughly correspond to better than 99% purity of the DNBS.

(1) 4.3 Blank Stock

A blank stock is used as the diluent for all calibration standards and sample dilutions. The blank stocks are prepared as outlined below. The weight tolerances are ±5% for each compound. These materials should have a minimum purity of 99%.

4.3.1 Diesel Blank Stock

This mixture is designed to simulate the boiling point range and density of diesel fuel, and is prepared by combining the following substances:

15 g tert-butylbenzene
15 g decane
15 g dodecane
15 g tetradecane
15 g hexadecane
15 g tetralin
5 g octadecane
5 g naphthalene

4.3.2 Gasoline Blank Stock

A similar blank stock is prepared for analyses of gasolines. This mixture is prepared by combining:

5 g n-pentane
10 g n-hexane
10 g cyclo-hexane
15 g n-heptane
20 g 2,2,4 trimethyl-pentane
10 g n-octane
5 g n-decane
15 g toluene
10 g mixed xylenes

(1) 4.4 Calibration Standards

Calibration standards are made from sulfur (DNBS) diluted in the appropriate blank stock in various concentrations. These standards are made up in sealed containers and are retained indefinitely.

4.5 Check Standard

The check standard is prepared in the same manner as the calibration standards, except that it need not be prepared in a sealed container, and is of a concentration that lies within the upper 50% of the active calibration curve. This standard is used only to verify calibration, not for the initial calibration itself. This standard is normally prepared in a larger quantity, e.g., 250 mL.

(1) 4.6 Control Fluid

The control fluid for each analysis is the current certification fuel, typically containing 0.03 to 0.05 weight percent sulfur for diesel, and 30 to 150 ppm sulfur for gasoline. The control fluids are used for routine quality control measurements. The control limits for these materials are established by control chart analysis of multiple sample analyses of the fuel.

(1) 4.7 Drift-Correction Fluid

The drift-correction fluid for the diesel analysis is a stable diesel fuel containing 0.15% to 0.20% (w/w) sulfur. This fluid is typically prepared by the addition of 13 mL of di-n-butyl-disulfide (practical purity) to 1 gallon of certification diesel fuel.

The drift correction fluid for the gasoline analysis is certification gasoline to which di-n-butyl-sulfide has been added in sufficient quantity to bring the sulfur concentration to between 1000 and 1500 ppm.

(1) 4.8 National Institute of Standards and Technology (NIST) Standard (for diesel fuel analysis)

This standard is made from sulfur in fuel oil, of suitable concentration for this analysis, and is principally used to ensure the accuracy of instrument calibration.

The NIST-determined concentration of this standard is used as the basis for quality control limits.

(1) 4.9 Independent Standard (for gasoline analysis)

Since no NIST standard is currently available for gasolines, an independent standard is made up by a different chemist or technician from the one making up calibration standards, using another sulfur source.

The independent standard is made by gravimetrically diluting thiophene (99% or better purity) or dibenzothiophene (99% or better purity) in gasoline blank stock. This standard is prepared in a manner exactly analagous to calibration or check standards (see step 7.4.)

Note: The weight fraction sulfur is 0.38103 for thiophene, or 0.17399 for dibenzothiophene.

4.10 Laboratory Supplies

4.10.1 Sample cups with plastic snap rings

4.10.2 Polypropylene film (0.2-mil)

4.10.3 5-mL automatic pipette and disposable pipette tips

4.10.4 1-, 5-, and 50-mL syringes and suitable needles

4.11 Helium, typically 99.99% purity, for the atmosphere of the analysis chamber

4.12 P-10 Gas

This is a mixture of 10% methane in argon blended specifically as a scintillation gas for x-ray detectors.

4.13 Analytical balance with an NIST-traceable calibration

200-g capacity, 0.1-mg resolution, or equivalent

4.14 Form 109-03, “Chain of Custody”

4.15 Environmental Protection Agency (EPA) Form 3500-5, “Fuels Field Inspection”

5. Precautions

(1) 5.1 Diesel fuel is flammable under some conditions. As a precaution, exposure to sparks and open flames should be minimized.

Gasoline is highly flammable. Exposure to sparks or flames must be eliminated.

5.2 Exposure to excessive quantities of x-ray radiation is injurious to health. X rays are ionizing radiation which, in large doses, will cause radiation sickness and death. The x-ray spectrometer should be operated in accordance with regulations and recommendations governing the use of ionizing radiation.

The operator must avoid exposing any part of his or her person, not only to primary x rays but also to secondary or scattered radiation that might be present. No maintenance is to be performed on the instrument when the x-ray source is on.

The x-ray unit must not be operated if any interlocks are open or if any radiation seals are suspected of being faulty.

A radiation badge must be worn when operating the x-ray unit.

5.3 Prior to performing the analysis, the analyst must be familiar with the Material Safety Data Sheets (MSDS) for materials used in this analysis.

6. Visual Inspection

6.1 Ensure that the samples do not contain sediment or separated phases prior to filling the sample cups.

If samples do contain sediments, they must be thoroughly mixed prior to analysis.

Multi-phase samples should have each phase analyzed separately if possible.

In both cases, the situation should be noted and initialed by the analyst on the instrument-generated sample analysis report (Attachments A and B.)

6.2 If the samples are for enforcement/litigation purposes, ensure that the sample bottles are tightly closed and labeled properly according to Form 109-03, “Chain of Custody” (COC), and ensure that the COC Forms are filled out properly. Note any discrepancies on the COC form.

6.3 If a sample is to be split and redirected to another laboratory or other location outside the present facility, a copy of the COC form will accompany this sample. It must be filled out to include all pertinent information and sent with the newly sealed sample. The original COC form is to remain in the Chem Lab files.

7. Test Article Preparation

7.1 Ensure that there are adequate quantities of helium and P-10 gas to complete the test sequence. At least 200 psi in all cylinders is prudent.

(1) 7.2 For normal operation in the analysis of sulfur in either fuel, the following settings and flow rates should be verified:

7.2.1 Ensure that a helium atmosphere is selected and that helium is flowing to the instrument at the specified flow rate of 1.0 L/minute.

7.2.2 Ensure that P-10 gas is flowing to the instrument at the specified flow rate of 50 mL/minute.

7.2.3 Ensure that the x-ray unit is on and operating at 30 kV and 80 mA.

7.2.4 Ensure that no warning messages are appearing on the instrument display.

(1) 7.3 Determine if instrument calibration is required. The following are guidelines for this determination:

Calibration will be necessary for a new instrument, or one not previously used for these analyses. Calibration will be required if current calibrations are lost or damaged. Calibration may be required after reconfiguration or repair of an existing instrument.

A new calibration may be necessary if the current check standard, control fluid, or NIST or independent standard results fall outside acceptance criteria.

If calibration is not required, proceed to Section 8 of this procedure.

If calibration is required, complete the remaining steps in Section 7.

Consult the laboratory supervisor if there are any questions regarding the need for a new instrument calibration.

(1) 7.4 Prepare the calibration standards. Standards are created by diluting pure DNBS with the appropriate blank stock. Standards are analyzed along with the blank stock used in making up standards, followed by a control-fluid sample, two instrument drift-correction-fluid samples, and the NIST or independent standard.

Standards should span the analytical range of interest. For typical enforcement testing of on-highway diesel fuel, five to eight standards should be spaced across the range of 0.005 to 0.500 weight percent.

For typical enforcement analyses of gasolines, five to eight standards should be spaced across 25 to 1500 ppm.

These values are reached by varying the mass of DNBS added to each standard vial. All dilutions are accomplished gravimetrically in septum-capped vials by the following procedure:

7.4.1 Select a 50-ml vial and crimp a pierceable septum onto it.

7.4.2 Ventilate the sealed vial with an appropriate needle. The needle is left in the vial cap.

7.4.3 Tare the empty, sealed vial and needle.

7.4.4 Introduce to the vial approximately 40 grams (approximately 48 mL) of the appropriate blank stock via syringe and needle.

7.4.5 Precisely weigh the vial. The display of the balance should give a reading corresponding to the mass of the blank stock present in the vial. Record this weight on the vial.

7.4.6 Retare the vial, complete with the vent needle and blank stock.

7.4.7 Add the appropriate amount of pure DNBS to the vial via a 1 mL syringe and needle. Each drop of DNBS will yield approximately a 0.01 increase in percent sulfur in the standard.

7.4.8 Precisely weigh the vial. This display will be a reading of the mass of DNBS added to the vial. Record this weight on the vial.

7.4.9 Remove the vent needle from the vial, and shake the vial to mix the contents.

7.4.10 Calculate the nominal concentration of sulfur in the vial.

For diesel fuel the weight percent sulfur is calculated as follows:

(mass DNBS)(weight fraction S)/(mass blank stock + mass DNBS) *100%

For gasoline the concentration of sulfur in ppm w/w is calculated as follows:

(mass DNBS)(weight fraction sulfur)/(mass blank stock + mass DNBS)*1,000,000ppm

In each equation, weight fraction S is the weight fraction of sulfur in the DNBS compound. If a DNBS compound of at least 99% purity is used, the weight fraction sulfur may be taken as 0.2191.

If a compound of less than 99% purity is used, the certified analysis provided by the chemical manufacturer must be used to calculate the true weight fraction sulfur.

Example: (0.2430g)(0.2191)/(39.1482g + 0.2430g)*100% = 0.1351 wt %

7.4.11 Label the vial with the calculated sulfur weight percent for diesel, or ppm w/w sulfur for gasoline, today’s date, and the analyst’s initials.

(1) 7.5 Transfer the standards, control fluid, drift-correction fluid, blank-stock solution, or samples to sample cups as follows:

7.5.1 Label the appropriate sample cups on the flat, outer section of the cup with the standard concentration (or sample number) using a permanent marker.

7.5.2 Since automatic pipettes and disposable tips are typically used for routine analysis, no cleaning procedure is required for their use with samples.

If glass pipettes or syringes are used, the cleaning procedure is to rinse the pipette or syringe with a suitable low-volatility pure hydrocarbon (e.g., dodecane for diesel and pentane for gasoline) and once with the sample that is to be transferred.

7.5.3 Beginning with the blank stock, and continuing with the lowest standard through to the highest, accurately pipette or syringe 5.0 ±0.1 mL of standard (or sample) into a clean sample cup.

When the automatic pipette is used, it must be kept in a vertical position during the transfer. During aspiration of sample, the end of the disposable tip should be immersed 2 to 3 mm below the liquid surface.

When gasolines are being analyzed, the best technique for use of the automatic pipet is to fill the pipet (in a vertical position), immediately empty the pipet back into the sample container, then refill the pipet. Since some of the sample is removed, then reintroduced to the sample container, a new pipet tip must always be used. This method helps minimize the evaporative loss that occurs during the initial filling of the pipet, and has been shown to improve precision. During this entire pipeting procedure, the pipet tip is maintained at 2-3 mm below the surface of the gasoline.

7.5.4 Place a polypropylene film over the sample cup. Secure the film in place with a plastic snap ring.

7.5.5 Make sure that there are no wrinkles in the film. If there are wrinkles, discard the sample and transfer a new aliquot to a fresh sample cup.

7.5.6 Invert the filled sample cup, and ventilate the cup by piercing a small hole in the top with a push pin or similar instrument.

7.5.7 Carefully place the sample cup film down on a piece of absorbent paper for several seconds to determine whether or not the film window is leaking.

If the sample container is leaking, discard the sample and prepare a new one.

(1) 7.6 Load the autosampler and check the instrument setup for the calibration run.

7.6.1 One sample cup of each calibration standard and the blank stock solution must be included in the set of calibration standards inserted into the autosampler.

7.6.2 The nominal concentration of each standard and its position in the autosampler must be input to the instrument controller, together with the code describing them as standards and a “7” in the “RPT” column for gasoline analyses.

Codes are readily available on the help screen in the analysis window of the software. Refer to the Rigaku Software Manual for additional details.

7.6.3 Each of these sample cups will be analyzed once, and only once, yielding a calibration intensity value.

7.6.4 Ensure that the instrument computer system date and time are correct.

7.7 Initiate the calibration analysis and perform the linear regression calculations according to the Rigaku Software Manual. For this calculation, a linear calibration fit should be used.

7.8 Following the completion of a calibration analysis and regression calculation, the calibration plot should be viewed to verify the linearity of the calibration. Any of the points that visually differ from linearity should be investigated.

Calculate the concentration of the calibration standards, based on the calibration line, and compare these values to the nominal concentration of the standards. The regression-determined concentration should be within ±5% of the nominal concentration. Investigate any points that do not meet this criterion. Failure to meet this criterion may mean that there was a problem in the dilution of one or more standards.

7.9 If the linearity of the calibration appears satisfactory, transfer an aliquot of the control fluid to a sample cup per Step 7.5, load it into the autosampler, and initiate analysis using the new calibration. The results from this analysis should be within the control fluid control chart limits.

If the results are not within these limits, the calibration is considered suspect, and the cause of the discrepancy must be resolved before the calibration can be accepted or samples analyzed.

7.10 If the data from the control fluid analysis appear satisfactory, transfer two aliquots of the drift correction fluid to sample cups per Step 7.5, load them into the autosampler, and initiate analysis. The first analysis is to be performed in an initial condition, and the second as an alpha standard. Refer to the Rigaku Software Manual for details of this setup. The result of this analysis will be an alpha-update value.

7.11 Check the alpha-update value. For this setup of the drift correction, the result would be suspect if this alpha value obtained were outside the range of 0.9 to 1.1. Values obtained on subsequent days may vary much more widely, but would be suspect if outside the range of 0.3 to 2.0.

(1) 7.12 If the result of the drift correction appears satisfactory, transfer an aliquot of the NIST standard (for diesel) or independent standard (for gasoline) to a sample cup per step 7.5, load it into the autosampler, and initiate analysis using the new calibration. The results from this analysis should be within ±3% of the named concentration of the standard**.**

(1) 7.13 If the data from the NIST or independent standard analysis appear satisfactory, the calibration must be saved within the data acquisition system.

7.13.1 The naming convention for saving a diesel calibration is the prefix SUL plus a sequential number. For example, the second calibration completed is named SUL2. The naming convention for gasoline calibrations is a prefix GAS followed by a sequential number. (Options for this naming convention are restricted by the software limit of four characters.)

7.13.2 After saving the calibration, a plot of the calibration should be printed, along with a list of the calibration parameters. These printouts, and the instrument-generated sample analysis reports for the control fluid and NIST or independent standard, must be saved in the notebook specific to the instrument. This notebook is stored in a secure place, normally in close proximity to the instrument.

7.13.3 Note the fact of a new calibration on the control fluid control charts.

8. Test Procedure

101 Obtain and inspect samples as described in the FCAB Enforcement Chain of Custody Procedure found in TP 109.

102 Place the sample in a sample cup using the technique described in Step 7.5.

103 Inspect each sample cup to verify that it is not leaking and to make sure that it is properly labeled.

(1) 104 For the first analysis performed each day, arrange the standards and test samples in the autosampler as described in the table below, and then input the sample and standard IDs to the Rigaku data system. Control fluid should be input as "Cert Diesel" or "Cert Gasoline" for ease in identifying the analyses.

Control fluid
Drift correction fluid (Alpha update)
Control fluid (Record result on Form 109-02)
Check standard
Up to 12 individual samples
Duplicate (Record result on Form 109-01)
Control fluid
Up to 12 individual samples
Duplicate (Record result on Form 109-01)
Control fluid
Sample
etc.
Control fluid (Record result on Form 109-02)

At least one check standard is analyzed each day testing is performed. The analytical session is always begun and completed with the control fluid.

Additionally, a control fluid sample and a duplicate are to be run at least once every 12 samples.

If the result of the initial control fluid analysis on a given day is within the control chart limits, the drift correction and subsequent control fluid analysis are unnecessary. In this situation, the initial control fluid analysis is recorded on Form 109-02.

105 Set up the autosampler to perform one analysis per sample cup. For this procedure, all analyses are to be run only once per sample cup. If a sample must be reanalyzed, prepare a new sample cup.

106 Check the instrument notebook to verify that the active calibration is the most recent calibration for this working range. Ensure that the instrument time and date are set correctly and initiate the autosampler per the manufacturer's instructions to begin the analysis.

107 As the results are produced, check to ensure that the detector is producing non-zero results for both the peak and background measurements.

Check the alpha value of the drift correction fluid. Alpha values following drift correction must be within the range of 0.3 to 2.0, except immediately following calibration, when they must be within the range of 0.9 to 1.1.

If the drift correction fluid results are not within these tolerances, investigate potential instrument problems. If the abnormal drift correction results can not be resolved, see the laboratory supervisor.

(1) 108 On Form 109-02, record and plot the result of the second (post-drift correction) control fluid analysis. Confirm that the sulfur concentration of the control fluid is within the appropriate control chart limits.

Investigate any out-of-control conditions and take immediate corrective action. Record the action and its implications on the control chart and repeat this step.

If out-of-control occurrences cannot be reconciled, consult the laboratory supervisor.

Initial the control chart in close proximity to the current entry, and save the chart in the instrument notebook.

Note: Subsequent charts should be placed behind the prior chart (if this is not the first) and following the current calibration printout. The instrument notebook is stored in a secure location near the instrument.

(1) 109 Confirm that the check standard result is within 5% of the calculated nominal concentration of that standard.

If the check standard is not within the ±5% limits, analyze a NIST or independent standard. If this standard is within 3% of its named value, discard the check standard and continue with the analysis. If the NIST or independent standard is out of specification, check for possible instrument malfunction, recalibrate the instrument and restart the analysis.

(1) 110 Confirm that the sulfur concentration of each subsequent control fluid analysis is within the control-fluid control chart limits. Record and plot the result of the last control fluid analysis of the session on Form 109-02.

If any control-fluid analysis indicates an out-of-control condition, halt the analysis and perform a drift correction. Record the action and its implications on the instrument-generated sample analysis report for the control fluid.

Repeat the control fluid analysis. If the post-drift correction analysis of the control fluid is acceptable, repeat the analysis of all samples run since the previous successful control fluid analysis. Discard the original results from these samples.

If out-of-control occurrences cannot be reconciled, consult the laboratory supervisor.

111 On Form 109-01, record and plot the absolute difference (range) between duplicate analyses.

Check that the range of the duplicates is within the control chart limits. For this procedure, these chart limits are defined as the 3-sigma confidence limit for the range of duplicates, based on acquired data.

If the duplicate range is out of control, halt the analysis and take immediate corrective action to resolve the abnormal analysis variability. Record the action and its implications on the control chart. If out-of-control occurrences cannot be reconciled, consult the laboratory supervisor.

When the problem is resolved, repeat the duplicate analysis and record and plot the results of this analysis on Form 109-01. Ensure that the results are within the control chart limits before proceeding with the analysis.

If the investigation indicates that an out-of-control occurrence may have affected previously analyzed samples, repeat the samples analyzed since the last acceptable duplicate analysis. Discard the original results from these samples.

Initial the control chart in close proximity to the current entry, and save the chart in the instrument notebook.

Note: Subsequent charts should be placed behind the prior chart (if this is not the first) following the current calibration printout. The instrument notebook is stored in a secure location near the instrument.

(1) 112 When the analysis batch has been completed, review the instrument-generated sample analysis reports to verify that all concentration values are within the working range of the current calibration.

If the analysis indicates that the sulfur concentration in any of the samples is greater than the calibration range, discard the original result and dilute the sample to fall within the calibration range. This is accomplished by w/w dilution with blank stock in a manner similar to that by which standards are prepared, except that the use of sealed vials is not necessary. (Refer to Step 7.4.)

When a sample must be diluted, the blank stock used for the dilution must also be analyzed with the diluted sample. For diesel analyses, the reported concentration of this blank stock must be below 0.002 weight percent sulfur for the diluted sample analysis to be valid. For gasoline analyses, the reported concentration of the blank stock must be below 10 ppm w/w sulfur.

If the analysis indicates a higher concentration of sulfur in the blank stock, discard the results from the diluted sample. A new batch of blank stock must be prepared and analyzed. If this blank stock yields a result of less than 0.002 weight percent sulfur for diesel analyses, or 10 ppm w/w sulfur for gasoline analyses, redilute and reanalyze the out-of-range sample(s).

If the dilute analysis is satisfactory, calculate the concentration of sulfur in the undiluted sample as follows:

$$S = S_b * [(W_s + W_o)/ W_s]$$

where: S_b = concentration of sulfur in diluted sample
W_s = weight of the original sample in grams
W_o = weight of the diluent in grams

This calculation must be shown on the instrument-generated sample analysis report for the diluted sample.

113 Check that the sample numbers on the instrument-generated sample analysis report match those on the sample cups in the autosampler. If this number is missing on the sample analysis report, it should be hand entered and initialed by the operator.

(1) 114 Discard the contents of used sample cups in the appropriate waste container.

9. Data Input

9.1 The identity of the sample cups and their autosampler position must be input to the data system before the start of each run. A report is generated by the Rigaku software for each analysis. The operator identifies each analysis and verifies that the printout contains the sample identification number written on the vial. If this number is missing on the printout, it should be hand entered and initialed by the operator.

9.2 If all acceptance criteria are met, the operator signs the report.

9.3 The analyst transfers sample results to Form 3500-5, the “Fuels Field Inspection” form.

9.4 Control fluid results from the first analysis following drift correction and last analysis are recorded and plotted on Form 109-02.

9.5 The results of duplicate analyses are recorded on Form 109-01.

10. Data Analysis

10.1 The spectrometer calculates the concentration of each sample based on the active calibration curve.

(1) 10.2 The analyst reviews the results of the control fluid, check standard (or NIST or independent standard), drift-correction fluid, and range of duplicate analyses for conformance to acceptance criteria.

10.3 If a calibration was performed, the analyst reviews the linearity of the curve and calculates the concentration of the calibration standards, based on the calibration line, and compares these values to the nominal concentration of the standards.

The results of the analyses of calibration standards, NIST standard, control fluid, and blank are reviewed for conformance to acceptance criteria.

(1) 10.4 If a sample dilution was required, the analyst checks the concentration of sulfur in the blank-stock solution. If that analysis conforms to the acceptance criteria, the concentration of sulfur in the undiluted sample is calculated as follows:

$$S = S_b * [(W_s + W_o)/ W_s]$$

where: S_b = concentration of sulfur in diluted sample
W_s = weight of the original sample in grams
W_o = weight of the diluent in grams

This calculation must be shown on the instrument-generated sample analysis report for the diluted sample.

10.5 The results are checked to ensure they have the proper sample ID number. If an error was made during log-in and was not corrected, then the results printout should show the correction. The analyst must initial and date any changes made to the instrument-generated sample analysis report

10.6 A verifying technician must compare the results entered on Form 3500-5 with the original instrument output for all non-compliant samples. Any discrepancies must be corrected, initialed, and dated.

10.7 If all acceptance criteria are met, the operator signs the instrument-generated sample analysis report. These reports are forwarded to the data filing area.

11. Data Output

11.1 The output from the analysis is an instrument-generated sample analysis report showing the various counting rates and the calculated concentration of each sample. This output is filed in the FCAB data filing area.

11.2 All results from samples diluted for analytical purposes must be clearly marked on the analysis report, describing the extent of dilution and the calculated concentration of the undiluted sample.

11.3 Sample results are transferred to Form 3500-5 and forwarded to the project officer.

(1) 11.4 If a new calibration curve is generated, a plot of the calibration and a list of the calibration parameters along with the calibration analysis results of the control fluid, drift correction fluid, and NIST or independent standard are filed in the notebook specific to the instrument.

11.5 Control fluid analyses and duplicate results are recorded on Forms 109-01 and 109-02 and are saved in a notebook specific to the instrument. This notebook is stored in a secure place, normally in close proximity to the instrument.

12. Acceptance Criteria

12.1 All points covered in Section 11 must be correct before the data for each run can be accepted.

12.2 All analyses of the control fluid bracketing the analytical session must be entered on the control-fluid control chart. These control charts must indicate that all samples were analyzed under conditions of known, stable accuracy.

12.3 Duplicate analyses must be entered on the applicable control chart. These control charts must indicate that all samples were analyzed under conditions of known, stable precision.

(1) 12.4 Check standards must be within ±5% of their nominal value. NIST or independent standards must be within ±3% of their nominal value.

12.5 The results sheets must be signed by the analyst and dated before the results can be filed.

12.6 Alpha values following drift correction must be within the range of 0.3 to 2.0, except immediately following calibration, when they must be within the range of 0.9 to 1.1.

12.7 When calibrations are performed, a plot of calibration standard concentration versus instrument response must not indicate any visible departure from linearity. The concentration of each standard as calculated from the regression line should be within ±5% of point of the nominal concentration of the standard.

(1) 12.8 If samples are diluted, analysis of the blank stock must indicate that the concentration of sulfur in the blank stock is less than 0.002% (w/w) for diesel or 10 ppm w/w for gasoline.

13. Quality Provisions

13.1 Visual inspection of samples and the instrument

13.2 Control fluid analysis before and after every 12 sample analyses to assess instrument drift

Drift correction performed as necessary

(1) 13.3 Analysis of external reference standards (NIST or independent standards) to assure accuracy of calibration

13.4 Analysis of laboratory duplicate samples to assure consistent precision

13.5 Analysis of calibration or check standards to verify instrument accuracy

13.6 Only one analysis is performed on each sample cup to minimize sample degradation.

13.7 Chain-of-custody provisions are followed to ensure sample integrity (for enforcement/litigation samples.)

Instrument-Generated Sample Analysis Report
(Diesel Fuel)

```
     P#   JOB  CODE    SAMPLE  NAME       LOT #                  94-04-28 14:06
 1-2 1:GRP SUL2 CERT DIESEL

                        S -KA
                        S

Peak   Int.   kcps    4.5160

BG     Int.   kcps    0.2778

Raw    Int.   kcps    4.2382

Net    Int.   kcps    1.5411

X-ray  Int.   kcps    1.5411

Results     S

          0.0335
```

Instrument-Generated Sample Analysis Report
(Gasoline)

```
P#   JOB   CODE    SAMPLE  NAME        LOT #              94-09-26 11:20
1-1 1:GRP GAS1 CERT GASOLINE

Meas. Int.    kcps    S -KA     S -KA     S -KA
                      S 20      S 20      S 20
                      Peak      BG01      BG02
    Repeat    =  1   1.5050    0.4360    0.1703
                 2   1.5154    0.4100    0.1708
                 3   1.5297    0.4473    0.1643
                 4   1.4974    0.4245    0.1678
                 5   1.5189    0.4283    0.1678
                 6   1.4745    0.4172    0.1641
                 7   1.5018    0.4152    0.1678

    Average          1.5061    0.4255    0.1676
    Maximum          1.5297    0.4473    0.1708
    Minimum          1.4745    0.4100    0.1641
    Range            0.0552    0.0373    0.0067
    Std. Dev.        0.01780   0.01297   0.00261
    C.V. %             1.18      3.05      1.56

P#   JOB   CODE    SAMPLE  NAME        LOT #              94-09-26 11:20
1-1 1:GRP GAS1 CERT GASOLINE

                       S -KA
                       S

Peak   Int.    kcps    1.5061

BG     Int.    kcps    0.2368

Raw    Int.    kcps    1.2693

Net    Int.    kcps    1.2691

Uncorrected Conc.        101.

Results     S

              101.
```